CLASSICAL THEORIES OF DIELECTRIC CONSTANTS

C. M. KACHHVA AND S. C. SAXENA*

PHYSICS DEPARTMENT, RAJASTHAN UNIVERSITY, JAIPUR, INDIA

(*Received October* 14, 1966)

ABSTRACT. The equivalence of the two classical theories of dielectric constant one due to Mott and Gurney and the other due to Szigeti is discussed and established. This consists in the suggestion to identify the effective charge of the ion in the Szigeti's model with a factor in the theory of Mott and Gurney which determines the degree to which the neighbouring ions overlap. The effective charge of the different alkali halide crystals has been recalculated on the basis of the first relation of Szigeti employing the more recent data for dielectric constants and Reststrahlen frequency. The second relation is employed to compute compressibility and these are compared with the latest experimental data. Our interpretation of the Szigeti's theory also permits the calculation of low frequency dielectric constant from its first relation. We also discuss a procedure for evaluating infrared polarizability values from the basic knowledge of interatomic forces. Lastly, we correct and complete some of the earlier reported results, (Kachhava *et al.* 1966) on the theory of Mott and Gurney.

INTRODUCTION

We (1966) recently discussed the possibility of calculating the dielectric constant through the knowledge of interatomic forces. For this purpose the theory of Mott and Gurney (1948) was considered and specific calculations were presented for the alkali halide crystals having the NaCl-type of structure. Unfortunately some numerical error inadvertently got associated with these calculations. The purpose of the present paper, though is to examine and discuss the theory of dielectric constant as formulated by Szigeti (1949,50), we find it necessary to briefly summarize the corrected results of our previous effort so that a proper appraisal of the new work may be possible.

In addition we discuss a procedure for calculating the infra-red polarizability from the basic knowledge of interatomic forces. We report here the computed values of the effective charge on the basis of the first relation of Szigeti (1949) and most recent data of dielectric constants and Reststrahlen frequency. A link between the theories of Szigeti (1949, 50) and Mott and Gurney (1948) is established by identifying the effective charge in the former theory with the factor γ which determines the degree to which the neighbouring ions overlap in the latter theory. This has enabled the computation of the low frequency dielectric constant ϵ_0 through the use of the first relation of Sziegeti.

*Present address: Thermophysical Properties Research Center, Purdue University, Lafayette, Indiana, U.S.A.

CALCULATION OF ATOMIC POLARIZABILITY

The familiar relation between the dielectric constant ϵ_0, and the polarizability α, is

$$\frac{\epsilon_0-1}{\epsilon_0+2} = \frac{4\pi\alpha}{3}. \qquad \text{... (1)}$$

Further if the crystal does not possess permanent dipole moment, α is composed of the infrared polarizability α_i, and the ultraviolet polarizability α_u, the latter being known from the Drude's relation. We have then the well-known Clausius-Mossotti equation,

$$\frac{\epsilon_0-1}{\epsilon_0+2} = \frac{\epsilon_\infty-1}{\epsilon_\infty+2} + \frac{4\pi}{3}\alpha_i, \qquad (2)$$

in which ϵ_∞ is the high frequency dielectric constant.

For rigid non-overlapping ions α_i is related with the force constant A, Dekker (1962),

$$\alpha_i \quad \frac{Ne^2}{A} \qquad (3)$$

Here N is the number of ions per unit cell, e the electronic charge and A is given by, Born and Huang (1956),

$$A = \frac{M}{3}\left[v''(r_0)+2\frac{v'(r_0)}{r_0}\right], \qquad (4)$$

M being the coordination number and r_0 the equilibrium inter-ionic separation. Furthr we (1966) suggested that an appropriate form for $v(r)$is,

$$v(r) = ae^{-r/\rho} - \frac{c}{r^6} - \frac{d}{r^8}. \qquad \text{... (5)}$$

Here a and ρ are the potential parameters, c and d the Van der Waals constants and r the interatomic separation.

We have now two ways of calculating α_i. One from Eqn. (2) with the knowledge of ϵ_0 and ϵ_∞, and another from Eqs. (3) to (5). The two sets of computed values are given in table I in columns 2 and 3. The values of ϵ_0 and ϵ_∞ are of Mott and Gurney (1948) and the details of the calculation of A are given by us (1966) earlier. The two sets of α values are in approximate agreement with each other and should be regarded as reasonable in view of the crude model and approximate nature of the theories.

TABLE I

The values of α_i, γ and s for alkali halide crystals

Crystal	α_i (10^{-24}cm^3)		γ		s
	Eq. (2)	Eq. (3)	Eq. (6)	Eq. (8)	
LiF	1.95	3.57	0.74	—	0.83
LiCl	3.26	4.51	0.68	0.54	0.74
LiBr	3.60	5.11	0.70	0.81	0.67
LiI	3.70	5.92	0.67	0.50	0.54
NaF	3.07	3.74	0.70	—	0.93
NaCl	3.35	4.77	0.70	0.37	0.74
NaBr	3.50	5.78	0.70	0.34	0.69
NaI	4.25	6.48	0.69	—	0.71
KF	3.66	4.50	0.74	—	0.91
KCl	4.13	6.34	0.71	—	0.80
KBr	4.29	6.74	0.69	0.25	0.76
KI	4.37	8.11	0.70	0.16	0.69
RbF	4.09	4.88	0.71	0.61	0.97
RbCl	4.90	6.52	0.71	0.37	0.84
RbBr	5.16	7.16	0.69	0.47	0.82
RbI	5.19	8.08	0.70	0.40	0.79
CsF	—	5.23	0.70	—	—
CsCl	5.46	6.99	0.72	0.68	0.84
CsBr	5.21	8.56	0.77	0.32	0.79
CsI	4.65	8.73	0.70	0.26	0.91

MOTT AND GURNEY THEORY OF DIELECTRIC CONSTANT

Mott and Gurney (1948) proposed that as a consequence of the overlap in the adjacent ions there is a reduction in the electric field due to polarization by a multiplicative factor γ. We (1966) have shown that

$$1-\gamma = \frac{\frac{r_0}{\rho} ae^{-r_0/\rho} - \frac{6c}{r_0^6} - \frac{8d}{r_0^8}}{e^2/r_0} . \qquad \ldots (6)$$

The computed values of γ for the twenty alkali halides are given in column 4 of Table I.

Mott and Gurney (1948) have given the following relation for the low frequency dielectric constant,

$$\frac{\epsilon_0-1}{3+(\epsilon_0-1)\gamma} = \frac{\frac{4\pi N}{3}(\alpha_1+\alpha_2)-\frac{32\pi^2}{9}N^2\alpha_1\alpha_2(1-\gamma)}{1-\frac{4\pi}{3}N(\alpha_1+\alpha_2)(1-\gamma)+\frac{16}{9}\pi^2N^2\alpha_1\alpha_2(1-\gamma)^2} + \frac{\frac{4\pi}{3}\delta}{1-\frac{4\pi}{3}\delta(1-\gamma)} \quad \ldots (7)$$

Here α_1 and α_2 are the polarizabilities of the two ions and $\delta = Ne^2/A$. An alternative form of this equation is

$$\frac{\epsilon_0-1}{3+(\epsilon_0-1)\gamma} = \frac{\epsilon_{cs}-1}{3+(\epsilon_{cs}-1)\gamma} + \frac{\frac{4\pi}{3}\delta}{1-\frac{4\pi}{3}\delta(1-\gamma)}. \quad (8)$$

Equation (8) is utilized to compute γ with the known experimental values of ϵ_0 and ϵ_∞ and of δ from Eq. (4). These values are recorded in column 5 of Table I. It is to be noted that this again tends to establish that Mott and Gurney theory of dielectric constant is inadequate to represent the facts.

Mott and Gurney (1948) also gave the following relation for the high frequency dielectric constant ϵ_∞ :

$$\frac{\epsilon_{cs}-1}{4\pi} = \frac{N(\alpha_1+\alpha_2)-8/3\,\pi N^2\alpha_1\sigma_2(1-\gamma)}{1-\frac{4\pi}{3}N(\alpha_1+\alpha_2)+\frac{16}{9}\pi^2N^2\alpha_1\alpha_2(1-\gamma^2)} \quad (9)$$

In the earlier work we (1966) reported ϵ_∞ values for all except Caesium halides. We have now calculated ϵ_∞ for these four halides employing the γ values as given by the relation of Eq. (6). These values also, like the remaining sixteen, are in good agreement with the experimental data. The average absolute deviation is 1.5 percent.

We now report the three sets of computed ϵ_0 values in Table II which supersede the earlier ones, Kachhava and Saxena (1966). In all calculations γ as obtained from Eq. (6) is used, while in the last it is identified with the effective charges as explained later. The other details are as given earlier by us (1966). We find that the relation of Eq. (7) is poor and inferior to that included in Eq. (8). We also notice that when γ is put equal to s the situation does not improve. All this simply confirms that the basic formulation is at fault.

SZIGETI THEORY OF DIELECTRIC CONSTANT

Szigeti (1949, 50) attempted to improve the Born's wellknown relation for ϵ_0 obtained on the assumption of non-deformable and non-overlapping ions, viz.

$$\epsilon_0 = \epsilon_{cs} + \frac{4\pi Nz^2c^2}{\mu w_0^2}. \quad \ldots (10)$$

TABLE II

The low frequency dielectric constant ϵ_0, of alkali halide crystals

Crystal	Experimental	Calculated		
		Eq. (7)	Eq. (8)	
			γ of Eq. (6)	$\gamma = s$
LiF	9.27	—	—	—
LiCl	11.05	21.5	13.9	15.1
LiBr	12.1	21.3	14.6	14.0
LiI	11.03	21.0	14.2	11.2
NaF	6.0	10.8	10.6	13.8
NaCl	5.62	8.75	7.05	7.29
NaBr	5.99	10.1	8.73	8.50
NaI	6.60	10.1	8.03	8.27
KF	6.05	8.30	8.65	5.43
KCl	4.68	6.72	6.26	6.72
KBr	4.78	6.36	6.20	6.47
KI	4.94	7.48	7.13	7.04
RbF	5.91	6.10	6.29	7.45
RbCl	5.0	5.79	5.67	6.19
RbBr	5.0	5.78	5.76	6.31
RbI	5.0	6.15	6.00	6.39
CsF	—	5.67	11.4	—
CsCl	7.20	7.52	7.49	8.46
CsBr	6.51	7.49	10.2	10.3
CsI	5.65	8.12	8.19	7.85

Here Z is the valency of the ions and μ the reduced mass of the two ions. He included the effect of the presence of other ions in the lattice and the fact that they overlap and cause deformation. He concludes that the net effect is that the dipole moment is reduced by a factor s and the Born's Eq. (10) assumes the following form as the first Szigeti's relation.

$$\epsilon_0 = \epsilon_{\infty s} + \frac{4\pi N s^2 z^2 e^2}{\mu w_0^2} \left(\frac{\epsilon_{\infty s}+2}{3} \right)^2. \qquad \ldots \quad (11)$$

Szigeti (1949) calculated the s values for the different crystals from Eq. (11) itself employing the experimental ϵ_0, ϵ_{cs} and w_0 values. We have repeated these calculations for all the alkali halides in conjunction with the most upto date experimental information. These are listed in column 6 of Table I.

Szigeti (1949, 50) has shown that there are several factors which control the magnitude of s. Hanlon and Lawson (1959) have however shown that the major contribution to s comes from overlap. Thus we find that the actual ionic charge Ze gets changed to sZe, an affective value, due to the interaction of the neighbouring ions. Further s is the measure of the reduction of the dipole moment and hence of polarization and consequently it also can be regarded as directly controlling the effective field which is due to polarization. It is now interesting

TABLE III

The values of w_0, β and ϵ_0 for alkali halide crystals

Crystal	$(10^{-13}s^{-1})$	βexptl	βcalc Eq. (12)	$\frac{\beta\text{calc}}{\beta\text{exptl}}$	ϵ_0 Eq.(11) with $s=\gamma$
LiF	5.73	1.49	1.55	1.04	7.83
Licl	3.84	3.36	3.69	1.10	10.7
LiBr	3.26	4.20	4.96	1.18	13.8
LiI	2.71	5.83	4.33	0.74	15.0
NaF	4.63	2.15	1.96	0.91	4.18
NaCl	3.09	4.17	4.68	1.12	5.13
NaBr	2.54	5.02	5.17	1.03	5.98
NaI	2.20	6.64	6.72	1.01	6.40
KF	3.62	3.28	2.98	0.91	4.36
KCl	2.71	5.73	5.04	0.88	4.31
KBr	2.18	6.75	5.97	0.88	4.36
KI	1.94	8.55	7.33	0.86	5.05
RbF	3.01	3.81	4.37	1.15	4.45
RbCl	2.24	6.40	5.73	0.89	3.75
RbBr	1.69	7.69	7.05	0.92	4.22
RbI	1.41	9.48	8.68	0.82	4.56
CsF	2.39	4.25	—	—	5.35
CsCl	1.86	5.55	5.12	0.92	5.05
CsBr	1.39	6.28	7.55	1.20	5.36
CsI	1.17	7.83	8.06	1.03	6.47

to recall that Mott and Gurney introduced the factor γ to take into account a similar effect. γ and s should therefore be identifiable with each other. This conclusion immediately provides a very pleasant correlating link between the two theories. This conclusion is indeed upheld by the records of columns 4 and 6 of Table I and many calculations of the properties described in this paper.

It is important to note that the s values vary between 0.70 to 0.95. The great success of the Born-Mayer theory of ionic crystals demands that s should not depart from unity by more than a couple of percent. Here we find the departure to be rather pronounced. In fact even Szigeti was quite alive to this trend and he has tried to explain it rather in detail. In passing we may however note as pointed out by Born and Haung (1956) that this anamoly is a consequence of simplifying in a crude fashion the physical picture involved in the phenomenon.

RELATION BETWEEN COMPRESSIBILITY, ϵ_0 AND ω_0

Szigeti (1950) in the further development of his theory derived a relation between compressibility β, ϵ_0 and w_0 which is now commonly known as his second relation. It is

$$\frac{1}{\beta} = \frac{r_0^2}{3v}\frac{(\epsilon_0+2)}{(\epsilon_{cs}+2)}\mu w_0^2 . \qquad \ldots (12)$$

In parallel with Szigeti's original approach we recalculate β using the recent data. The w_0 values in particular are recorded in Table III column 2. The β values so obtained are listed in column 4 of this very Table. These should be compared with the experimental isothermal β values also recorded in this very Ttable in column 3. To make this comparison explicit we quote in column 5 the ratio β calc/β expt. It will be seen that though in a few cases the disagreement is pronounced, yet on the whole the facts are well reproduced. This study pro vides a quantitative assessment of the success of Szigeti's theory and must be regarded as fairly en- courating.

CALCULATION OF ϵ_0

We again put a test to the Szigeti's theory on the basis of first relation, Eq. (11). The approach is unconventional in asmuch as it uses the suggestion developed in this paper of equating s with γ. Under this limitation the computation of ϵ_0 from Eq. (11) is straightforward when for all the other quantities we employ the experimental information. These values are recorded in column 6 of Table III. The deviations between the computed and experimental values are given in column 7. The agreement is certainly very encouraging when one notes that the average absolute deviation is only 10.2 percent for all the alkali halide crystals. This also provides an indirect proof for ascertaining the s values through γ and their complete equality.

CONCLUSIONS

We thus find that amongst the classical theories of dielectric constant Mott and Gurney theory fails to reproduce the experimental information, while that Szigety theory is successful to a large extent. These detailed calculations performed for all the twenty alkali halide crystals and with the use of the latest experimental data provide the necessary background against which the more recent theories can be assessed. We do not mention any such details here but plan to report them in a separate article. These detailed and elaborate calculations, Kachhava (1966), simply tend to improve our faith in the Szigeti's theory to approximately understand the dielectric phenomenon inasmuch as the new values differ in general by a nominal amount and one further finds that these sophisticated calculations cannot be easily extended to all alkali halide crystals.

REFERENCES

Born, M. and Huang, K., 1956, *Dynamical Theory of Crystal Lattices*, Clarendon Press, Oxford.

Dekker, A. J., 1962, *Solid State Physics*, MacMillan and Co. Limited, London.

Hanlon, J. E. and Lawson, A. W., 1959, *Phys. Rev.*, **113**, 472.

Kachhava, C. M., 1966, *Ph.D. Thesis : Certain Problems of Solid State Physics*, Rajasthan University.

Kachhava, C. M. and Saxena, S. C., 1966, *Indian J. Phys.* **40**, 225.

Mott, N. F. and Gurney, R. W., 1948, *Electronic Processes in Ionic Crystals*, Clarendon Press, Oxford.

Szigeti, B., 1949, *Trans. Faraday Soc.* **45**, 155.

———, 1950, *Proc. Roy. Soc.* (*London*) *A***204**, 51.